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Ultrasound-assisted oxidative desulfurization/ denitrification of liquid fuels with solid oxidants

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KEYWORDS: Ultrasound reactors; Clean fuels; Oxidative desulfurization; Oxidative denitrification; Oxone[®].

ABSTRACT. The restrictions placed on the ultra-low sulfur content of diesel fuels by stringent legislation have instigated the search for alternative cost-effective and complimentary methods for the deep desulfurization of fossil fuel derived oil. Current technology for oxidative fuel desulfurization/denitrification is hampered by mass transfer efficiency, post-treatment purification and process costs. Owing to their mild operative conditions, ultrasonic-assisted oxidative desulfurization (UAOD) processes are currently a hot investigation topic. In this piece of work we have applied UAOD to two model compounds: dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) as well as to a mild hydro-treated diesel feedstock using a number of different solid oxidants including Oxone[®], sodium persulfate and potassium superoxide. The oxidized organic sulfur compounds (sulfones) were

extracted using a suitable polar solvent or adsorbent. Oxone[®] was the most efficient of all the solid oxidants tested under high-intensity ultrasound. After 30 min sonication, this protocol enabled the consistent reduction of S and N content in treated diesel to less than 10 ppm and 2 ppm respectively.

1. INTRODUCTION

The presence of sulfur compounds in fuels (thiols, sulfides, disulfides and thiophenes) is still the largest source of SO_x and sulfate particulate matter (SPM) emissions into the atmosphere. These all contribute to acid rain, air pollution and endanger public health and the environment.^{1,2} In recent years, many countries have introduced more stringent regulations in an effort to reduce the sulfur levels in fuel oil to ultra-low levels (10-15 ppm).³ As a consequence, the removal of sulfur from transportation fuel is extremely important in the petrochemical industry and the development of deep desulfurization technology for the production of ultra-low sulfur fuel oil has become a huge target for worldwide researchers. Most organosulfur compounds are generally removed from hydrocarbon fuels by high temperature (300-400°C) hydrodesulfurization (HDS) that operates at high hydrogen pressures (20-100 bar) over CoMo/Al₂O₃ or NiMo/Al₂O₃ catalysts.⁴ Although the HDS process can effectively remove aliphatic and acrylic sulfur compounds such as thiols, sulfides and disulfides, some S-heterocycles such as benzothiophene (BT), dibenzothiophene (DBT), and their alkyl derivatives, 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), are quite refractory to this treatment.^{5,6} This limitation can be attributed to both the steric hindrance of the aromatic sulfur species and to the high electron density around the sulfur atom. Therefore, conventional hydrotreatment must be modified and revamped if it is to produce ultra-low sulfur diesel (ULSD).⁷ In the last few decades, alternative deep desulfurization techniques have been extensively investigated, these include; extractive desulfurization (EDS), which can even make

use of task specific ionic-liquids;^{8,9} adsorptive desulfurization (ADS);^{10,11,12} oxidative desulfurization (ODS);¹³ and bio-desulfurization (BDS).^{14,15} ODS has perhaps drawn the most widespread attention,¹⁶ because of its mild operative conditions (atmospheric pressure, <100°C) and the fact it proceeds without hydrogen consumption. This process generally involves two steps; oxidation^{17,18} followed by extraction.¹⁹ The greatest advantage of this process is the fact that sulfur compounds that are refractory in HDS, such as alkyl benzothiophenes, are easily oxidized to sulfoxides or sulfones in high yields in ODS.²⁰ The higher polarity of sulfur oxides means that these compounds are easily removed from hydrocarbons by solvent extraction (NMP, DMF, DMSO and MeOH),²¹ or solid adsorption (silica, alumina, zeolites and metal organic frameworks).²² ODS is thus a complementary process to classic HDS in producing deeply desulfurized light oil. Hitherto, many oxidizing agents have been investigated, which include organic and inorganic peroxyacids, catalyzed hydroperoxides, *t*-butyl-peroxide, nitrogen oxides, ozone and some O₂/aldehyde/transition metal (Co, Ni) systems.²³ Peracids are widely exploited because of their high reactivity. However, there are some drawbacks to scaling-up a peracid based ODS procedure. These compounds are highly corrosive and instable and so have to be produced in situ by hydrogen peroxide and carboxylic acid (formic acid or acetic acid). Hydrogen peroxide is not a common feedstock in refinery plants; the price is relatively high and storage of large amounts entails safety concerns. Moreover peracid based ODS processes are two-phase reaction systems. Mass transfer limitations make this reaction too slow for industrial use and would warrant phase transfer catalysts,²⁰ microemulsions²⁴ or microstructured reactors.²⁵ However, optimal mass transfer across the interphase can be achieved under mild reaction conditions using UAOD.²⁶⁻³² For a heterogeneous liquid-liquid reaction system such as fuel ODS, both the physical and chemical effects of acoustic cavitation influence reaction kinetics

and yield. Intense microturbulence, created by cavitation, generates radicals in the medium due to the extreme conditions of temperature and pressure (~ 5000 K and ~ 500 bar) generated in the bubble at transient collapse, it disrupts the liquid/liquid interface and creates a very fine emulsion between the phases.^{33,34} In fact, most published UAOD studies have focused on liquid-liquid biphasic systems.³⁵ In this piece of work, three different solid oxidants have been tested: Oxone[®], sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and potassium superoxide (KO_2), which have been used both in the oxidation of a model sulfur compound (DBT) and on a mildly hydro-treated diesel feedstock ($\text{S} = 226 \pm 2.17$ ppm; $\text{N} = 158 \pm 2.81$ ppm). Classic UAOD with H_2O_2 / acetic acid was also carried out for comparison.

2. EXPERIMENTAL SECTION

2.1 Materials

Reagents, oxidizing agents (Oxone[®], sodium persulfate and potassium superoxide) and model sulfur (DBT and DMDBT) and nitrogen (quinoline) compounds were all purchased from Sigma Aldrich - Italy. Silica gel 60 by MERCK (0.063-0.200 mm) was used for column chromatography. Hydro-treated diesel feedstock (S and N content of 226 ppm and 158 ppm respectively) was provided by PETROBRAS (Brazil).

2.2. Instruments

UAOD experiments were performed in two different ultrasonic devices: a cup-horn like cavitating tube (Danacamerini - Italy) working at 19.9 kHz and a probe system with a titanium horn (Danacamerini - Italy) working at 21.1 kHz. US power, reaction time and temperature were

defined as follows: 80 W, 90 min and 80°C. Experiments were carried out in batch mode and under temperature control. Tests under mechanical stirring (350 rpm) were carried out for comparison with US.

2.3. Analysis

The treated DBT, DMDBT and quinoline model solutions (in toluene) were analyzed by GC-MS (gas-chromatograph Agilent 6890 with mass detector Agilent Network 5973) using a 30 m long capillary column, i.d of 0.25 mm and film thickness 0.25 μ m. Temperature program: from 80°C (3 min) to 300°C at 5°C/min.

Sulfur and nitrogen elemental analyses of fuel samples were performed by Multi EA[®] 5000 Analytik Jena - Germany, in accordance with national and international standards (ASTM D 5453 and D 4629). Fuel samples viscosity and density were measured with the viscometer Stabinger SVM 3000 (Anton Paar GmbH, Graz, Austria), according to ASTM D 7042-04.

Diesel oil acidity was determined using the titration system Titrando 836, (Metrohm, Herisau, Switzerland) equipped with a magnetic stirrer (module 803 Ti Stand), 20 mL burette (Dosino 800) and pH electrode (LL Electrode plus, model 6.0262.100).

2.4. General procedures

2.4.1 Techniques

Oil bath (OB): stirring at 350 rpm, 80°C, time 10 to 90 min.

US horn: 21.1 kHz, 80 W, 80°C, time 10 to 90 min.

US cup horn: 19.9 kHz, 80 W, 80°C, time 10 to 90 min.

2.4.2 Procedures

Oxone[®]: Diesel samples and DBT or DMDBT (1.2 mg/ml) model solutions (25 ml) were oxidized with Oxone[®]. S+N: Oxone[®] tested molar ratios were:

- 1 : 10 = 25 ml : 2.66 g
- 1 : 20 = 25 ml : 5.32 g
- 1 : 30 = 25 ml : 7.96 g.

Na₂S₂O₈/CH₃COOH: Diesel samples and DBT or DMDBT (1.2 mg/ml) model solutions (25 ml) were oxidized with a mixture of Na₂S₂O₈ that had previously been dissolved in water and glacial acetic acid.

S+N : Na₂S₂O₈ : CH₃COOH tested molar ratios were:

- 1 : 10 : 63 = 25 ml : 1.03 g in H₂O (2 ml) : 1.55 ml
- 1 : 20 : 126 = 25 ml : 2.06 g in H₂O (3.5ml) : 3.11 ml
- 1 : 30 : 190 = 25 ml : 3.08 g in H₂O (5 ml) : 4.69 ml.

KO₂/CH₃COOH: Diesel samples and DBT or DMDBT (1.2 mg/ml) model solutions (25 ml) were oxidized with a mixture of KO₂ and glacial acetic acid.

S+N : KO₂ : CH₃COOH tested molar ratios were:

- 1 : 10 : 69 = 25 ml : 0.306 g : 1.72 ml

- $1 : 20 : 139 = 25 \text{ ml} : 0.613 \text{ g} : 3.43 \text{ ml}$
- $1 : 30 : 208 = 25 \text{ ml} : 0.92 \text{ g} : 5.13 \text{ ml}$.

H₂O₂/CH₃COOH: Diesel samples and DBT or DMDBT (1.2 mg/ml) model solutions (25 ml) were oxidized with a mixture of hydrogen peroxide and glacial acetic acid.

S+N : H₂O₂ : CH₃COOH tested molar ratios were:

- $1 : 10 : 198 = 25 \text{ ml} : 0.257 \text{ ml (50\% wt)} : 4.88 \text{ ml}$
- $1 : 20 : 396 = 25 \text{ ml} : 0.513 \text{ ml (50\% wt)} : 9.76 \text{ ml}$
- $1 : 30 : 594 = 25 \text{ ml} : 0.77 \text{ ml (50\% wt)} : 14.64 \text{ ml}$.

2.4.3 Reaction workup

For the model solutions, the oxidized organic phase was washed with water (3 x 15 ml), dried with anhydrous Na₂SO₄ and, after paper filtration, analyzed by GC-MS.

In the case of Oxone[®], the reaction mixture (solid/liquid) was directly filtered on paper and analyzed by GC-MS.

For diesel oxidation, two different workup methods were performed:

- oxidized diesel (2 ml) was filtered on silica gel (1.2 g) and then analyzed with the N/S elemental analyzer.
- oxidized diesel (2 ml) was shaken in a separating funnel with MeOH (2 ml) and then analyzed with the N/S elemental analyzer.

3. RESULTS AND DISCUSSION

3.1. Characterization of the raw materials

UAOD with solid oxidants is underexploited because of critical mass transfer. In this present work, the effect of US in solid/liquid heterogeneous systems is evaluated, using different types of solid oxidants. DBT, DMDBT and quinoline solutions were used as model S and N compounds respectively, with KO_2 , $\text{Na}_2\text{S}_2\text{O}_8$ and Oxone[®] so as to create a better comparison with typical liquid/liquid oxidation using peracetic acid. The optimized protocols were repeated with the mild hydro-treated diesel feedstock. The effect of acoustic cavitation was evaluated by comparing the results achieved with the protocols described in Table 1 with tests performed in an oil bath (OB) at the same time under mechanical stirring (350 rpm) without US.

Table 1 Oxidation of DBT (model solution in toluene) by sonochemical activation.^a

| Entry | Oxidant | Time (min) | Yield ^b (%) | | |
|----------------|-----------------------------------|---------------|------------------------|-------------------------|-----------------------------|
| | | | OB | US horn ^c | US cup horn ^d |
| 1 | $\text{H}_2\text{O}_2^{\text{e}}$ | 9 | 42 | 89 | 93 |
| 2 | KO_2^{e} | 15 | 68 | 97 | 95 |
| 3 | Oxone [®] | 90 | 0 [0] ^f | 100 [100] ^f | 100 [100] ^f |
| | | | [0] ^g | [40] ^g | [42] ^g |
| 4 ^h | Oxone [®] | 90 | 0 [0] ^f | 99 [100] ^f | 98 [100] ^f |
| | | | [0] ^g | [38] ^g | [40] ^g |
| 5 | $\text{Na}_2\text{S}_2\text{O}_8$ | 45 | 0 | 4 | 2 |

| | | | | | |
|---|------------------------------------------------------------|----|----|----|-----|
| 6 | Na ₂ S ₂ O ₈ ^e | 45 | 97 | 99 | 100 |
|---|------------------------------------------------------------|----|----|----|-----|

^a Molar ratio S : oxidant = 1 : 10

^b DBTO + DBTO₂

^c US at 21.1 kHz, 80 W, 80°C

^d US at 19.9 kHz, 80 W, 80°C

^e In the presence of CH₃COOH

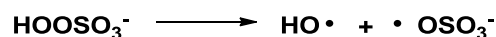
^f Yield referred to DMDBT oxide

^g Yield referred to quinoline oxide

^h Molar ratio S:oxidant = 1:3

According to the literature,³¹ a peracetic acid system generated *in situ* by both H₂O₂ and KO₂ with acetic acid has given excellent results. Clearly the instability of peracetic species and their corrosive nature are critical points for large scale applications. Indeed, it is possible to reach high conversions to sulfones in a short time with this system (9-15 min), while a longer time is required with OB.

Oxone[®], a triple potassium salt (2 KHSO₅, KHSO₄, K₂SO₄) was the most versatile oxidizing agent. Its active component is potassium monopersulfate (KHSO₅), which is a salt of Caro's acid (H₂SO₅). The oxidation potential of peroxymonosulfate-bisulfate couple (E° = 1.44 V) is able to oxidize aliphatic and aromatic sulfides.



Scheme 1 Formation of reactive radical species.

Oxone[®] has found many applications thanks to its high stability and oxidation power,³⁶ and can also be applied to sulfoxidation reactions, generally in aqueous solutions of

acetone or methanol. Oxone[®] is completely insoluble in toluene and magnetic stirring under conventional heating only weakly activated the “peroxidation” reaction. In fact, both DBT and DMDBT were not oxidized after 90 min at 80°C. While, complete conversion occurred after 90 min under US at the same temperature. Furthermore, Oxone[®] worked in a quasi-stoichiometric ratio. Persulfate also gave good results, but it requires the addition of acetic acid to fully maximize its oxidation power. These data have shown that only Oxone[®] works without acetic acid in a short time under US and that it also represents a valid alternative for the oxidation of N-compounds in neutral conditions (about 40% of quinoline oxide under US in 90 min at 80°C).

The investigation was then extended to the UAOD of diesel feedstock (S and N 226 ± 2.17 ppm and 158 ± 2.81 ppm respectively). The cup horn device was selected as the US reference tool for these experiments. The residual S and N content in oxidized diesel was detected by an elemental analyzer after the workup which consisted in the S and N oxidation products being generally removed from treated diesel by liquid-liquid extraction using a polar solvent such as MeOH or by SiO₂ adsorption. The results reported in Table 2 show that these systems provide high levels of desulfurization. While 90% desulfurization can be reached in only 10 minutes with liquid oxidants, solid oxidants required longer times (90 min) to give the same results. Furthermore, the influence of the diesel (S+N): oxidant molar ratio was much more evident with the solid oxidant than with the liquid.

Adsorption onto SiO₂ was more efficient in separating the oxidized S-compounds, but the diesel mass loss was higher than in liquid/liquid extraction (96% diesel recovery with MeOH extraction *vs* about 85% with SiO₂ adsorption). Oxone[®] showed comparable

activity to liquid oxidant systems and avoids the addition of CH_3COOH . With a molar ratio of (S+N) diesel : oxidant = 1 : 30, 94% desulfurization was achieved in only 30 minutes (after SiO_2 adsorption).

The oxidative treatment did not affect the diesel physical properties. Density, viscosity and acidity values were comparable with those of untreated diesel (table 3).

Diesel UAOD in a cup horn with excess Oxone[®] was efficiently oxidized for 4 treatment cycles without the need to add additional amounts of Oxone[®] (Table 4). In each subsequent reaction the reacted liquid phase (diesel) is leaked out of the reactor and the solid Oxone[®] was left in the bottom of the US device.

Table 2. UAOD of diesel (S=226 ± 2.17 ppm N=158 ± 2.81).^a

| Oxidant | Ratio (S+N:Oxidant) | Yield ^b (%) | | | | | |
|------------------------------------------------------------|------------------------|------------------------|------|------------------|------|------------------|------|
| | | 10 min | | 30 min | | 90 min | |
| | | SiO ₂ | MeOH | SiO ₂ | MeOH | SiO ₂ | MeOH |
| H ₂ O ₂ ^c | 1:10 | 90 | 49 | 95 | 61 | 98 | 71 |
| | 1:20 | 92 | 64 | 98 | 76 | 99 | 79 |
| | 1:30 | 93 | 73 | 99 | 77 | 99 | 79 |
| Oxone [®] | 1:10 | 62 | 33 | 72 | 42 | 96 | 57 |
| | 1:20 | 89 | 38 | 92 | 43 | 99 | 60 |
| | 1:30 | 88 | 60 | 94 | 61 | 99 | 65 |
| Na ₂ S ₂ O ₈ ^c | 1:10 | 87 | 23 | 96 | 23 | 98 | 38 |
| | 1:20 | 65 | 23 | 73 | 28 | 99 | 38 |
| | 1:30 | 90 | 23 | 93 | 28 | 99 | 43 |
| KO ₂ ^c | 1:10 | 82 | 33 | 85 | 43 | 88 | 49 |
| | 1:20 | 92 | 36 | 96 | 43 | 97 | 57 |
| | 1:30 | 96 | 49 | 98 | 61 | 99 | 67 |

^a Using cup horn (19.9 kHz, 80 W, 80°C)^b Desulfurization^c In the presence of CH₃COOH

Table 3. Physical parameters of the diesel before and after the oxidative treatment.

| Condition (S+N:Oxone) | Density (g cm ⁻³ , 20°C) | Viscosity (mm ² s ⁻¹ , 40°C) | Acidity (mg KOH g ⁻¹) |
|---------------------------------|-----------------------------------------------|--------------------------------------------------------------|---------------------------------------------|
| Untreated | 0.8683 ± 0.0003 | 4.3165 ± 0.0054 | < 0.02 |
| 1:10 | 0.8670 ± 0.0008 | 4.3177 ± 0.0049 | < 0.02 |
| 1:20 | 0.8639 ± 0.0011 | 4.3167 ± 0.0114 | < 0.02 |
| 1:30 | 0.8628 ± 0.0009 | 4.3171 ± 0.0127 | < 0.02 |

About 5-8% Oxone[®] remained in suspension in the diesel phase after each cycle as the treated diesel was recovered from the US reactor by simple decantation. This drawback can be avoided by centrifugation or filtration.

Table 4 Oxone[®] recycling

| Cycle | Workup | Desulfurization yield (%) |
|--------------|------------------|--------------------------------------|
| 1 | MeOH | 59 |
| | SiO ₂ | 84 |
| 2 | MeOH | 61 |
| | SiO ₂ | 86 |
| 3 | MeOH | 66 |

| | | |
|---|------------------|----|
| | SiO ₂ | 87 |
| | MeOH | 79 |
| 4 | SiO ₂ | 95 |

In our protocol the suspended Oxone[®] was removed from treated diesel together with the oxidized S and N compounds via simple work up with MeOH or SiO₂. This investigation proves that an Oxone[®] excess can be reused in several cycles without any degradation or loss in activity which is an important finding in view of potential diesel UAOD up scaling.

The protocols used in this work also showed efficient denitrification, whether with or without acetic acid, achieving levels of about 1 ppm (see supporting information).

4. CONCLUSIONS

An efficient sonochemical protocol that uses Oxone[®] in the oxidative desulfurization/denitrification of liquid fuels has been developed. Although this ODS and ODN protocol is superior to any other batch process, the general drawback of there being two-phases is the loss in diesel mass that currently makes this approach under-competitive with respect to the classic catalytic hydrotreating process. However, thanks to the strong mechanical/chemical effects of acoustic cavitation, it can certainly be applied as a complementary strategy for conventional HDS treatment. This protocol enables a consistent reduction of S and N content in treated diesel to less than 10 ppm and 2 ppm respectively, in 30 min using a (S+N) diesel :

oxidant molar ratio of 1:30, while also simplifying final diesel purification by filtration onto SiO₂. The final goal of S concentrations of below 1 ppm appears to be in sight.

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